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ELUCIDATION OF ELECTROCHEMICAL REACTIONS AND SYSTEMS

SUMMARY OF PROGRESS
FOR YEAR ENDING 30 JUNE 1962

By

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Released by

CHEMISTRY DIVISION, RESEARCH DEPARTMENT



NAVAL ORDNANCE LABORATORY CORONA
CORONA, CALIFORNIA

NAVAL ORDNANCE LABORATORY CORONA

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FOREWORD

This document reports the work performed during fiscal year 1962 under the supervision of Professor Charles W. Tobias, Head of the Department of Chemical Engineering of the University of California at Berkeley, in accordance with the terms of a contract with the Naval Ordnance Laboratory Corona. Except for slight changes in format and very minor editorial changes, the report is as submitted to the NOLC Chemistry Division by Dr. Tobias.

The author has included a list of technical reports. These reports will be available upon request to Code 441, U. S. Naval Ordnance Laboratory, Corona, California; they should not be requested from the contractor. The theses mentioned in the report may be obtained through the University library.

The work represented herein was performed under NOLC Contract N123(62738)23531A, and was authorized under WepTask RMMO-22-030/211-1/F009-08-001.

C. J. HUMPHREYS
Head, Research Department

ABSTRACT

Projects reported for fiscal year 1962 are concerned with reference electrodes for liquid ammonia systems, oxidation potential of calcium in thiocyanate-liquid ammonia solutions, and theoretical analysis of current distribution in porous electrodes. Studies in progress include physical properties of metallic solutions of ammonia, and electrode reactions in solutions of inorganic salts in dimethyl sulfoxide.

INTRODUCTION

The NOLC contract calls for the elucidation of the electrode reactions, in liquid ammonia solutions, of several electrode-electrolyte combinations, and for investigations leading to new electrochemical systems for potential use as reserve power supplies.

EQUIPMENT AND APPARATUS¹

After two years of continuous service, the refrigeration compressor had to be rebuilt in November 1961. At the same time a number of improvements were incorporated in the layout of the vacuum line. A third vacuum system was added to the existing two, to allow preparation of anhydrous substances. Details were given in the Quarterly Letter Report of April 1962.

Between January and March 1962 the entire laboratory was moved into new rooms in Gilman Hall, which were specifically prepared to accommodate electrochemical research and the handling of work in nonaqueous solvents. Investigations were resumed at the normal rate in April 1962.

For the purification of certain nonaqueous solvents, a distillation column (5 cm diameter, 1 m long) with reflux control has been installed. For solubility and conductance studies, a constant-temperature bath with suitable shakers for solubility apparatus was constructed. A variety of conductance cells were built, and a high precision bridge was designed and constructed.

¹Ed. Note: The refrigeration equipment has been described in detail in "Investigation of Electrochemical Processes in Liquid Ammonia," an M.S. thesis written by G. D. Snider; and a description of the equipment and procedures for measuring the equilibrium potentials and polarization of calcium electrodes was given in a Ph.D. thesis, "Studies on the Anodic Behavior of Calcium in Liquid Ammonia," by F. E. Rosztoczy.

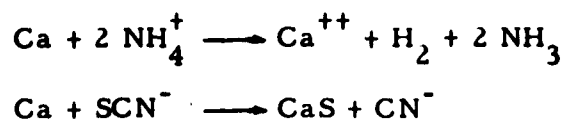
EXPERIMENTAL AND THEORETICAL RESULTS

Reference Electrodes

The suitability of a 0.1N lead/lead nitrate electrode as a reference for potential measurements in the presence of 20 mol% ammonium thiocyanate was ascertained by investigations with cells of 0.1N concentration versus 0.01N concentration over the temperature range -35 to -70°C and for periods up to 140 hr. Overall potential reproducibility of ± 2 mv and stability of ± 0.2 over several minutes were obtained. Potassium thiocyanate, ammonium nitrate, and sodium nitrate can be used instead of ammonium thiocyanate with equal results. In the lead/lead sulfide/sodium sulfide system, various surface treatment procedures could not eliminate instability and deviations from reversible potential. The silver/silver thiocyanate/ammonium thiocyanate electrode showed close to reversible potential; however, the stability and reproducibility were found unsatisfactory.

Chemical Dissolution of Calcium in Thiocyanate-Liquid Ammonia Solutions

In NH_4SCN solutions, calcium reacts according to the stoichiometric equations



In neutral KSCN solutions, all calcium reacts according to the second equation, forming S^{--} and CN^- . A reaction mechanism was proposed which takes into account the rate the dissolution decreases as the thiocyanate concentration increases.

Electrochemical Dissolution of Calcium

From crude polarization data obtained at -34°C in 20 mol% $\text{NH}_4\text{SCN-NH}_3$ solutions containing 0.1N $\text{Ca}(\text{NO}_3)_2$, the value of the corrosion current was found to be 24-41 ma/cm^2 . This range of values is in reasonable agreement with the rate of chemical dissolution of Ca in the same solution: 0.7 mol/hr cm^2 or 36 ma/cm^2 .

Oxidation Potentials of Calcium in Liquid Ammonia

Potentials of a $\text{Ca}/0.1\text{N Ca}(\text{NO}_3)_2$ electrode were measured at -34°C against a $\text{Pb}/0.1\text{N Pb}(\text{NO}_3)_2$ electrode. Values are as follows:

	<u>Volts</u>
With no thiocyanate present	2.04
With 20 mol% NH ₄ SCN	2.184
With 20 mol% KSCN	2.17

The effect of 20 mol% ammonium thiocyanate on the potentials of other metal couples (Mg, Zn, Cd) was found to be negligible. The low value found for Ca in the absence of thiocyanate is attributed to rapid corrosion by direct reaction of Ca with the solvent. Setting

$$E^0_{\text{Pb/Pb}^{++}} = 0$$

2.184 v is regarded as the best value to date for the oxidation potential of Ca in liquid ammonia.

Metallic Solution of Ammonia

Saturated metallic solution of Ca (in NH₃) containing 20 mol% NH₄SCN demonstrated a stable oxidation potential relative to a Pb/Pb⁺⁺ reference electrode—2.184 ± 0.005 v at -40°C—which corresponds within experimental accuracy with the value obtained for the solid metal in the same electrolyte. Because of the potential interest in metallic solutions for battery purposes, a literature search was conducted on properties of metal-ammonia solutions. It revealed substantial gaps in knowledge about the essential characteristics of the metallic solutions of the earth alkali series.

Investigations in Other Nonaqueous Solvents

On the basis of continued search for solvents of potential interest for high energy electrode reactions, dimethyl sulfoxide was selected for closer scrutiny. Its good stability, high dielectric constant (47), and Trouton's constant (29), together with findings in polarographic work, appear to justify exploratory studies of solubilities, conductances, and electrode reactions in this solvent. For removal of impurities, treatment with Al₂O₃, followed by fractional distillation, is being used at present. Initial results on stability with respect to strong oxidizing or reducing conditions are encouraging.

Analysis of the Behavior of Porous Electrodes

Theoretical analysis of the current distribution of porous electrodes using a model analogous to a linear distributed conductor has been completed. The model included the consideration of Tafel polarization and mass transport of the reacting ionic species in the steady state. Preliminary analysis of transient phenomena in porous electrodes has also

been undertaken. Extension of these studies to detailed analysis of single pores and to experimental verification of theoretical results is now in progress under the sponsorship of the National Aeronautics and Space Administration.

Studies on Ionic Mass Transport and the Nature of Gas-Electrolyte-Electrode Interfaces

The effects of combined natural and forced convection on transport rates were investigated, using optical observation techniques. The existence of helical roll-flow has been demonstrated on horizontal cathodes facing upward in the gravitational field. A literature search was conducted on the detailed processes involved in the behavior of gas-electrolyte-electrode surfaces. By agreement with the sponsoring agency, since April 1962 these two projects are being supported by Advanced Research Projects Agency funds administered by the Army Signal Corps.

FUTURE WORK

The program under the present contract will concentrate on investigations related to metal-ammonia solutions, and on the characteristics of other potentially useful nonaqueous media. The following investigations are planned for the immediate future:

1. Essential physical properties of metal-ammonia solutions (primarily those of calcium) will be measured, and the possibility of application of these solutions as liquid anodes will be explored.
2. Solubilities and conductances of various inorganic salts will be measured in purified dimethyl sulfoxide. Certain electrode reactions of interest in nonaqueous battery systems will also be studied.

REPORTS, THESES, AND PAPERS

Results of work carried out under this contract are published in the form of M. S. and Ph.D. theses, and when it appears justified, in the form of Internal Technical Reports directed to the Electrochemistry Branch of the Naval Ordnance Laboratory Corona.

Reports and Theses

In fiscal year 1962, the following reports and theses were written:

Technical Report No. 2: "Studies on the Anodic Behavior of Calcium in Liquid Ammonia." Ph.D. thesis by F. E. Rosztoczy, December 1961.

Technical Report No. 3: "A Model for the Analysis of Porous Electrodes." M. S. thesis by J. S. Newman, December 1961.

Internal Technical Report: "Studies on Reference Electrodes with Ammonia as a Solvent," by R. H. Muller, 15 July 1961.

Internal Technical Report: "Transient Phenomena in the Discharge of Porous Electrodes," by J. S. Newman, 12 March 1962.

Translations

The following translations of important foreign references were provided for the NOLC laboratory:

"Physical Processes in the Pores of Plates During the Discharge of a Lead Storage Battery with Large Current Densities." Ph.D. thesis by Werner Stein, 1959. Translated by John Bomben, 13 April 1962.

Translations of two other papers, which reached the University laboratory in preprint form, were also provided to the NOLC laboratory. Because these papers have not been published as yet, the translations are regarded as confidential and therefore are not listed here.

Papers

The following papers were prepared for presentation at technical meetings:

At the Fourth Symposium on Ammonia Batteries, 25-26 January 1962, Berkeley, California:

"Reference Electrodes for Battery Purposes," by R. H. Muller.

"The Oxidation Potentials of Calcium in Liquid Ammonia," by F. E. Rosztoczy.

"Theoretical Analysis of Current Distribution in Porous Electrodes," by J. S. Newman.

At the 121st National Meeting of the Electrochemical Society, 6-10
May 1962, Los Angeles, California:

"Reference Electrodes for Liquid Ammonia Systems," by A.
Dammers, R. H. Muller, G. D. Snider, and C. W. Tobias.

"Oxidation Potential of Calcium in Thiocyanate-Liquid Ammonia
Solutions," by F. E. Rosztoczy and C. W. Tobias.

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